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RAMAN SPECTROSCOPIC STUDY OF THE RARE EARTH SESQUISULFIDES

by

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Raman Spectroscopic Study of the Rare Earth Sesquisulfides*

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Abstract: Raman spectra have been measured on carefully synthesized and characterized sesquisulfides of the rare earth ions plus yttrium and scandium. Six structure types are represented. The Raman spectra are diagnostic of the structures type. Raman line widths indicate structural disorder only in the defect gamma type structure. High wavenumber bands shift with ionic radius of the rare earths and only slightly with cation coordination number.

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INTRODUCTION

The sesquisulfides of the rare earths exist in six different crystallographic forms depending on temperature of synthesis and ionic radius of the rare earth. The structures and crystal chemistry have been studied intensively particularly by Flahaut and his colleagues [1-6]. Because of the range of crystal structures and coordination polyhedra of the rare earth ions, it is of interest to examine the vibrational spectra of these compounds. The spectra may then be compared with the vibrational spectra of related ternary rare earth-containing sulfide structures, [7,8].

EXPERIMENTAL METHODS

The rare earth compounds were purchased from Cerac, Inc. X-ray powder diffraction patterns were obtained to determine which structure was represented and to determine phase purity. All compounds were fired for 24 hours at 1000 C in an atmosphere of flowing H_2S . This treatment converted any oxidized or hydrolysed material to sulfide and also improved the crystallinity. The sulfides did not hydrolyse or oxidize rapidly under laboratory ambient. It was possible to handle the compounds and measure their spectra in the open atmosphere.

The high temperature gamma polymorph was obtained by sealing the low temperature form in evacuated silica tubing and heating for 48 hours at 1300 C. The epsilon structures, Yb_2S_3 and Lu_2S_3 also gave clean x-ray diffraction patterns after they had been heated to 1300 C for 24 hours in evacuated sealed silica tubes or in flowing H_2S .

Raman spectra were obtained using an Instruments SA, Ramanor U-1000 microfocus spectrometer. The samples were measured as powders dispersed on a microscope slide at the focal point of the microscope attachment. The

632.8 nm line of a He-Ne laser was the excitation source. Because the band gaps of these materials range from 2.3 to 2.8 eV [9], resonance enhancement of the Raman scattering allowed good spectra to be obtained with a 15 mw laser, amounting to 0.7 mw at the focal point. Five or more scans were taken of each sample; these were coadded to increase signal to noise ratio. The spectra reproduced in this paper were taken directly from the plotter of the instrument control computer.

RESULTS

Structural information on the rare earth sesquisulfides is summarized in Table 1. The Greek letter notation introduced by Flahaut is retained. The alpha, beta, and delta structures are unique whereas the gamma, epsilon, and tau structures belong to established structure types as indicated on the table. Capital letter notations have also been suggested [10]. However, it has long been customary to refer to the structures of the rare earth oxides as the A, B, and C types and the sulfides are not isostructural with the oxides. Overall, it appears to be less confusing to retain the Greek letter notation.

As expected, there are strong similarities between the Raman spectra of compounds belonging to the same structure type. The spectra and their description are, therefore, arranged according to structure.

The Alpha Structure

The alpha structure was determined by Prewitt and Shannon [11]. It consists of a three-dimensional framework of interlocked GdS_7 and GdS_8 polyhedra. Factor group analysis (Table 2) predicts 30 Raman lines.

Raman spectra of alpha structure compounds (Fig. 1) show a relatively sparse pattern of bands. There are a few intense lines with a larger



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number of weak ones. The total number of lines observed above background is only about one third of the predicted number. It was not possible to prepare α - La_2S_3 completely free of the beta structure and its spectrum is not shown. The most intense features are very similar to the spectra in Fig. 1.

The three high wavenumber bands, which are likely Ln-S stretching modes, vary in a nearly linear fashion with rare earth ionic radius (Fig. 2). The slopes of the three lines are very similar. Band wavenumber decreases with increasing ionic radius, thus longer bonds and smaller force constants, but increases with increasing atomic weight of the rare earth ion.

The Beta Structure

The beta structure appears mainly as an oxysulfide with the formula $\text{Ln}_{10}\text{S}_{14}\text{O}_x\text{S}_{1-x}$. The 15th sulfur anion occupies a unique structural position [13] and it alone can be replaced by oxygen. There is a solid solution as indicated in the formula but there has been argument whether or not the pure sulfide end member ($x = 0$) exists. We found that minuscule amounts of oxygen were sufficient to stabilize the beta structure. Although the beta structure of the larger rare earths was easily synthesized, it was not certain that any of the preparations were oxygen-free. Accordingly, we do not report a spectrum here.

The beta structure has a large and complex unit cell leading to the prediction of 93 Raman lines. Raman spectra of the oxysulfides usually contain less than 20% of the predicted lines although the lines are very sharp and the spectrum complex. The entire problem of the stability of the beta structure and its spectrum is discussed elsewhere [14].

The Gamma Structure

Ln_2S_3 compounds belong to the cubic Th_3P_4 structure type. The cations occupy the 12(b) equipoints and the anions the 16(c) equipoints. There are four formula units in the unit cell. For compounds such as CaLa_2S_4 and SrNd_2S_4 which also belong to the Th_3P_4 structure the 16 S-atoms occupy the 16(c) sites and $\text{Ca} + 2\text{La}$ (or $\text{Sr} + 2\text{Nd}$) occupy the 12(b) sites. All sites are exactly filled and there are no vacancies. However, because the cations sites contain divalent and trivalent cations on the same site, there is an intrinsic disorder which leads to the broadening of certain of the Raman lines of the otherwise ordered compounds [7].

It is apparent from the chemical formula, Ln_2S_3 , that there are too few atoms to fill the equipoints and thus the γ - Ln_2S_3 compounds must be defect structures. One defect structure has balanced cation and anion vacancies: $\text{Ln}_2 \square \text{S}_3 \square$. However, some crystallographic evidence has been offered that the anion site is filled and that the formula should be written as $\text{Ln}_{2.67} \square_{0.33}\text{S}_4$ [10].

The spectra for four compounds with the gamma structure are shown in Fig. 3. These were obtained by coadding 10 - 15 individual scans. The spectra are very similar from one compound to another with five broad bands easily recognizable. Band wavenumbers decrease linearly with increasing ionic radius. Calculations for the gamma structure [7] give A_1 (Raman) + 2 A_2 (inactive) + 3 E (Raman) + 5 T_1 (inactive) + 5 T_2 (IR + Raman) in factor group T_d . Analysis of the cation and anion sublattices indicates that the A_1 mode contains only motions of the S-atoms and does not involve the cations. Thus only anion vacancy disorder would contribute to the broadening of this mode. In compounds of the type MLn_2S_4 , the $230\text{-}250\text{ cm}^{-1}$ band is much sharper than the others, as would be expected if the anion

sites were completely filled. This band may be assigned to the A_1 mode in the gamma structure. In the Raman spectra of the solid solutions along the join $\text{SrNd}_2\text{S}_4 - \text{Nd}_2\text{S}_3$, the band width of the A_1 mode increases abruptly from 8 cm^{-1} to 16 cm^{-1} at $x = 0.4$ [15].

The $230 - 250 \text{ cm}^{-1}$ band in the Raman spectra of the gamma structures is somewhat narrower than the other bands but it is still very broad compared with the Raman lines of the other sesquisulfide structures. We conclude from the results in Fig. 3, that there are vacancies on both cation and anion sublattices. The Raman spectra do not support the model with a completely filled anion sublattice.

The Delta Structure

Ho_2S_3 is the prototype compound based on the structure analysis of White et al. [16]. Half of the rare earth ions are in 6-fold coordination and half are in 7-fold coordination. The primitive monoclinic cell contains 6 formula units. Factor group analysis (Table 3) predicts 45 Raman-active modes.

The spectra of delta-structure compounds are complex (Fig. 4) but the lines are very sharp and of various intensities. Somewhat more than half of the predicted lines are observed. However, given the number of lines, accidental overlaps and weak bands lost in the background are to be expected. The narrow lines indicate a highly ordered structure. The broad intense feature near 400 cm^{-1} in the Ho_2S_3 spectrum is a luminescence band. The Raman spectrum of Y_2S_3 is very similar to the spectra of the rare earth sesquisulfides except for some small wavenumber shifts.

The Epsilon Structure

The epsilon structure of the rare earth sesquisulfides is isostructural with the corundum structure found widely in oxide materials.

The prototype is Al_2O_3 for which detailed single crystal Raman spectra have been measured [17]. The classification of normal modes is $2 A_{1g}$ (Raman) + $3 A_{2g}$ (inactive) + $5 E_g$ (Raman) + $2 A_{1u}$ (inactive) + $2 A_{2u}$ (IR) + $4 E_u$ (IR). Seven Raman lines are expected in the powder spectra.

Only the two smallest rare earth ions take on the 6-coordination of the epsilon structure. The spectra (Fig. 5) consist of six sharp lines. The 252 cm^{-1} band appears as a sharp line in the Lu_2S_3 spectrum but as a broad band centered at 234 cm^{-1} in the Yb_2S_3 spectrum. Samples of Yb_2S_3 from different sources with and without a pretreatment firing in H_2S all produced the same spectra. This rather odd feature appears to be real. All other lines have corresponding shapes in the spectra of the two compounds.

The pattern of lines in the corundum structure sulfides matches in only a rough way the pattern of lines in corundum structure oxides. The triplet of high wavenumber lines appears in both sulfide and oxide spectra but the wavenumbers of the sulfide lines are much lower than would be expected from scaling by the reduced masses, suggesting that the force constants of the thiocorundum compounds are substantially lower than the oxide corundum compounds.

The Tau Structure

Sc^{3+} is not a rare earth ion but its crystal chemistry is often similar to rare earth crystal chemistry although the ionic radius is distinctly smaller, 87 pm. The structure of Sc_2S_3 was called the tau structure by Flahaut and co-workers. It is isostructural with one of the structures of the sesquioxides of the rare earths, the C-type rare earth oxide or bixbyite structure. The bixbyite structure has a large and complex cubic unit cell with all cations in 6-fold coordination although

there are two cation sites with different site symmetries. The factor group is T_h . The normal modes have been classified [18] as $4 A_g$ (Raman) + $4 E_g$ (Raman) + $14 T_g$ (Raman) + $5 A_u$ (inactive) + $5 E_u$ (inactive) + $16 T_u$ (IR).

Figure 6 shows the spectrum of Sc_2S_3 . The Raman lines are sharp and well defined but only 11 of the predicted 22 modes are observed. The pattern of bands is very similar to that of the isostructural oxide but with wavenumbers shifted to lower values by a factor of approximately the square root of the sulfur to oxygen mass ratio.

DISCUSSION AND CONCLUSIONS

The Raman spectra of the sesquisulfides of the rare earths and similar ions occur in distinct patterns related to the structure type of the rare earth. These patterns are similar to the spectra patterns for isostructural oxides only in a general way. Metal-sulfur bonding is sufficiently different from metal-oxygen bonding that there are substantial differences in bond force constants in addition to the mass differences. In general, band wavenumbers decrease with increasing ionic radius (decreasing atomic number) for any series of rare earth ions within the same structure type.

With the exception of the gamma structure, all Raman lines have band widths on the order of $3 - 5 \text{ cm}^{-1}$, typical of well-ordered compounds. Band widths in the spectra of the gamma structures are on the order of $20 - 40 \text{ cm}^{-1}$, representative of disordered structures with randomly distributed vacancies. It was concluded that the Th_3P_4 structure was achieved in the Ln_2S_3 compounds by a distribution of vacancies on both cation and anion sites.

There is a small average decrease in mean vibrational wavenumber with increasing coordination number. However, unlike certain families of ternary sulfides [8], the trend is weak and except for the 8-coordinated gamma structure, the mean of the wavenumbers of the bands above 200 cm^{-1} decreases only slightly with increasing coordination number. The variation between compounds is larger than the variation between structures. With regard to the application of these compounds as IR window materials, except for the gamma structure, there is no benefit in first order phonon wavenumber from one structure to the next.

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TABLE 1. Structures of the Rare Earth Sesquisulfides

Notation	Symmetry	Space Group	z	Cation Coordination**	Structure Type
α	Orthorhombic	$Pnma$	4	8-7	Gd_2S_3 Type
β^*	Tetragonal	$I4_1/acd$	8		---
γ	Cubic	$I\bar{4}3d$	4	8	Th_3P_4 Type
δ	Monoclinic	$P2_1/m$	6	7-6	Ho_2S_3 Type
ϵ	Trigonal	$R\bar{3}c$	2	6	Corundum Type
τ	Cubic	$Ia\bar{3}$	16	6	Bixbyite Type (C-Type Rare Earth Oxide)

* Usually written $Ln_{10}S_{14}^{0}S_{1-x}$

** "8-7" etc. indicates two cation sites with different coordination numbers

TABLE 2. Factor Group Calculation for the α Structure

D_{2h}	Acoustic	Vibrations	Selection Rules
A_g	-	10	Raman
B_{1g}	-	5	Raman
B_{2g}	-	10	Raman
B_{3g}	-	5	Raman
A_u	-	5	Inactive
B_{1u}	z	9	IR, E c
B_{2u}	y	4	IR, E b
B_{3u}	x	9	IR, E a

TABLE 3. Factor Group Calculation for the δ Structure

C_{2h}	Acoustic	Vibrations	Selection Rules
A_g	-	30	Raman
B_g	-	15	Raman
A_u	z	14	IR, $E \parallel b$
B_u	x, y	28	IR, $E \perp b$

Legends for Figures

- Fig. 1 Raman spectra for powdered rare earth sesquisulfides with the alpha structure. Asterisks indicate plasma lines.
- Fig. 2 Relation of band wavenumber to cation radius for alpha structures. Sulfide crystal radii for 8-coordination from Shannon [12].
- Fig. 3 Raman spectra for powdered rare earth sesquisulfides with the gamma structure.
- Fig. 4 Raman spectra for powdered rare earth sesquisulfides with the delta structure. Asterisks indicate plasma lines.
- Fig. 5 Raman spectra for powdered rare earth sesquisulfides with the epsilon structure. Asterisks indicate plasma lines.
- Fig. 6 Raman spectrum of Sc_2S_3 with the tau (bixbyite) structure. Asterisks indicate plasma lines.











